

Nickel and chromium in wastewater – The Malaysian experience

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ABSTRACT

Heavy metals in natural water bodies pose a serious problem in Malaysia. Ni and Cr have drawn particular attention owing to their prevalence in various industrial effluents. While efforts are being made by industries to control discharges by recycling the metals, a lack of cost effective technologies appear to be a constraint. This paper discusses these issues in Malaysian and global perspectives.

Keywords : Nickel and chromium, Industrial effluents, Recycling, Heavy metal pollution.

INTRODUCTION

There has been a growing concern in Malaysia about pollution of heavy metals in water. Industries such as electroplating, metal finishing, circuit board production and so on contribute large amount of heavy metals as pollutant to the environment^[1]. Metal finishing industry produce a large quantity of heavy metals as waste^[2,3]. In addition to heavy metals these waste streams contain acids, bases, solvents and oils. Table 1 shows the typical waste components found in metal finishing industries and Table 2 shows the characteristic of the wastewater in Malaysia.

Industries are the major source of metal pollution in rivers^[6]. A study on tissues of fishes collected from the downstream of heavy industries further suggests that industries mostly contribute heavy metals in wastewater^[7]. The Water Quality Monitoring Program of the DOE in 1992 confirmed that heavy metal pollution in rivers was due to industrial activities^[8]. The degree of heavy metal pollution is still on the rise, although several Acts and Regulations have been enacted to control the pollution.

Table 1 : Metal finishing operations and typical wastes ^[4]

Source	Waste
Degreasing	Solvents, oils
Cleaning	Alkalis, metals, chelates, solvents
Pickling	Acids, metals, chromates
Metal plating	Acids, metals, cyanide, alkalis, chelates
Etching	Metals, acids, chelates
Conversion coating	Chromate, phosphates, metals

Table 2 : Characteristics of Metal Finishing Wastewater ^[5]

Metal Finishing Operation	Some Common Constituents
Acid pickling bath	Fe, Cu, Zn, Ni, Cd
Alkaline pickling and cleaning bath	Al, Zn
Acid and alkaline plating bath	Cu, Zn, Ni, Sn, Cd
Chromic acid-based bath	Cr, Al, Zn, Cd
Phosphoric acid-based bath	Fe, Zn, Mn
Metal polishing bath	Cu, Ni, Fe, Al
Cyanide solutions	Cu, Zn, Cd, other precious metals

VARIOUS TECHNIQUES OF TREATMENT TECHNOLOGY

There are various techniques for separating heavy metals from effluents generated by industries. The physico - chemical treatment which is the conventional technology employed to treat heavy metal waste includes chemical precipitation, ion exchange, evaporation and membrane technology ^[9].

Chemical Precipitation

The removal of heavy metals can be accomplished by chemical precipitation processes, in which metal ions in solution are converted to a solid phase, or sludge by the addition of chemicals. The sludge, usually insoluble hydroxides, are dewatered and stabilized prior to sending for disposal. It is important to neutralize the pH of the effluent, so that metal hydroxides are produced ^[10]. The yield of insoluble precipitates from this neutralization is dependent on the concentration of heavy metals in the effluent and the pH. Each metal has an optimum pH at which it will almost completely precipitate ^[11]. The sludge formation in high volumes which is difficult to dispose, leads to the generation of hazard-

ous pollutants. In Malaysia, it was found that 15% of the waste generated in 1987 represents sludge with heavy metals ^[3]. Further more, the use of stabilizing agents such as cement and fly ash before the sludge disposal increases the disposal cost dramatically ^[12].

Ion Exchange

Ion exchange is a process in which mobile ions are held by electrostatic forces to the solid surface of the resin and the exchanged ions from the resin become mobile and go into solution. Ion exchange resins are made in the form of very small spheres or beads, so that when packed in columns, they present an enormous surface area to the effluent and each bead has on its surface thousands of functional groups ^[13]. Ion exchange resins can be regenerated so that they can be used over and over again. Cationic resins are regenerated by mineral acids. Ion exchange can only remove ionized species and it requires a large volume of resins for treatment of high metal ion concentration in effluents. It also generates high concentration of salt residue ^[4]. The presence of divalent calcium and magnesium in higher concentrations in electroplating wastewater can compete with the heavy metals for the binding sites on the resins. The binding of these ions to the resins limits the removal of heavy metals from the wastewater ^[12].

Evaporation

Evaporation is the oldest method used to recover metals from electroplating wastewater. Most electroplating solutions and most pre and post plating process solutions require regular additions of chemicals to replace materials which are lost as drag-out. As a process evaporation is energy intensive but produces effluent with low metal concentrations and meets the discharge standards ^[4].

Membrane Separation

A membrane can be viewed as a semi-permeable barrier between two phases. This barrier can restrict the movement of molecules across it in a very specific manner. This barrier can be solid, liquid, or even a gas. The semi-permeable nature of a membrane ensures that separation takes place. The manner in which the membrane restricts molecular motion can take many forms. The size exclusion, differences in diffusion coefficients, electrical charge and differences in solubility are some examples.

There are two important aspects in this definition. First, a membrane is defined based on what it does, not what it is ^[14]. Secondly, a membrane separation is a rate process. The separation is accomplished by a driving force, not by equilibrium between phases ^[15]. The driving forces are either pressure,

Table 3 : Membrane Separation and Applications ^[16]

Membrane Separation	Driving Force	Applications
Microfiltration	Hydrostatic Pressure	Clarification, sterile filtration
Ultrafiltration	Hydrostatic Pressure	Separation of macromolecular solutions
Nanofiltration	Hydrostatic Pressure	Separation of small organic compounds and selected salts from solution
Reverse Osmosis	Hydrostatic Pressure	Separation of microsolute and salts from solutions
Gas Permeation	Hydrostatic Pressure, Concentration Gradient	Separation of gas mixtures
Dialysis	Concentration Gradient	Separation of microsolute and salts from macromolecular solutions
Electrodialysis	Electrical Potential	Separation of ions from water and non-ionic solutes

concentration, temperature or electrical potential. In many cases the transport rate (permeation) is proportional to the driving force and the membrane can be categorized in terms of an appropriate permeability coefficient. Table 3 lists the more industrially important membrane processes and their applications.

The use of driving force as a means of classification is not altogether satisfactory because apparently different membrane processes can be applied for the same separation, for example, electrodialysis, reverse osmosis and pervaporation in the desalination of water. From the point of view of applications, classification made in terms of suspended solids, colloids or dissolved solutes, etc. is preferred (Fig.1).

Reverse Osmosis

Reverse osmosis is a pressure driven process. The transport mechanism is primarily solution-diffusion rather than sieving action of microfiltration and ultrafiltration ^[17]. Reverse osmosis rejects particles as small as 10^{-3} to 10^{-4} μm , which include ionic materials and dissolved salts ^[16]. Usually, reverse osmosis process operates on the concept of crossflow filtration. Pressure in the system forces water through the membrane. The concentrated or rejected solution is

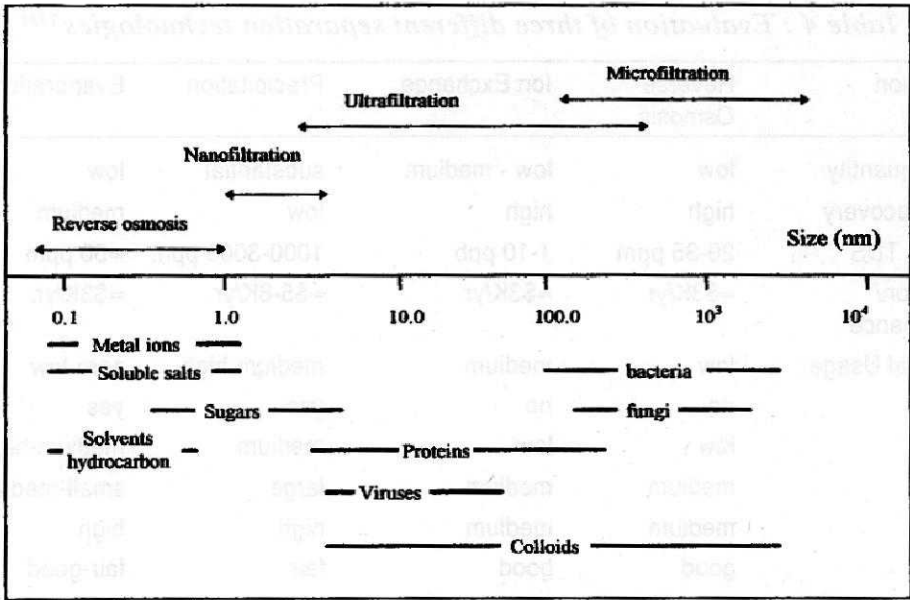


Figure 1 : Application size range of membrane filtration processes.

usually recycled to the process ^[11]. The different types of membrane modules commonly used in the reverse osmosis process are: (i) tubular, (ii) spiral-wound, (iii) hollow fiber and (iv) plate and frame.

Among these, spiral - wound units are not easily plugged by suspended solids, have minimum concentration polarization, minimum contamination and high pressure durability. It is the most widely used configuration in the reverse osmosis technique ^[18]. Three types of semipermeable membrane materials can be used in reverse osmosis units: (i) cellulose acetates (acetate, diacetate and triacetate), (ii) aromatic polyamide and (iii) thin film composite membranes.

Reverse osmosis membranes are sensitive to pH. However, thin film composite membranes are least affected by pH (ranges from 1 to 12) and is commonly used in manufacturing membranes. The recovery of nickel from rinse waters has been the most successful application of reverse osmosis. In waste nickel baths, reverse osmosis can recycle 99% of the drag-out nickel salts to the plating bath. The recovery of chromium from low pH chromic acid rinse water is now possible with the application of a thin film composite membrane which has wide pH range ^[19]. The reverse osmosis process, as applied in electroplating industry, is capable of achieving zero discharge in certain applications. There can be no detrimental environmental impacts associated with this technology provided the reject stream is recycled. When properly applied, reverse

Table 4 : Evaluation of three different separation technologies ⁽¹¹⁾

Evaluation	Reverse Osmosis	Ion Exchange	Precipitation	Evaporation
Waste quantity	low	low - medium	substantial	low
Water recovery	high	high	low	medium
Effluent TDS	20-35 ppm	1-10 ppb	1000-3000 ppm	≈50 ppm
Operation/ maintenance	≈\$3K/yr.	≈\$3K/yr.	≈\$5-8K/yr.	≈\$3K/yr.
Chemical Usage	low	medium	medium-high	zero-low
Permit	no	no	yes	yes
Energy	low	low	medium	medium-high
Space	medium	medium	large	small-medium
Labour	medium	medium	high	high
Overall	good	good	fair	fair-good
Capital Costs and Capacity	\$30-40K 20 litres/min.	\$25-40K 20 litres/min.	\$40-65K 20-50 litres/min.	\$20-40K 200-400 litres/hr.

osmosis systems should also achieve economic benefits associated with chemical recovery and the reduction of the expense of hazardous waste disposal ⁽¹³⁾.

Comparison of Different Methods

A comparative study on three different method of heavy metal treatment has been done by Chang ⁽¹¹⁾. The study involves the technical and economic analyses of reverse osmosis, ion exchange and precipitation processes, which are summarized in Table 4. The total annual cost includes the cost of operation and maintenance, labour, chemicals, permitting and regulatory compliance and waste disposal ⁽¹¹⁾.

THE EFFECT OF CHROMIUM

In natural deposition, chromium is found mainly in trivalent state. Naturally occurring hexavalent chromium has also been found. Chromium is present mainly in spinel-type minerals such as iron and magnesium chromo-aluminates, and as chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). Chromite ores are mostly mined in the former USSR, South Africa, Albania, Zimbabwe and Philippines. Alloy steels usually contains about 10-26% Cr. The refractory properties of Cr are exploited in the production of refractory bricks for lining furnaces and kilns, which accounts for approximately 15% of the chromate ore used. General chemical industries such as chrome

Table 5: Some uses of chemicals containing chromium ^[20]

Antifouling Pigments	Metal Finishing
Antiknock Compounds	Metal Primers
Catalysts	Mordant
Ceramics	Phosphate Coatings
Corrosion Inhibitors	Photosensitisation
Drilling Mud	Pyrotechnics
Electronics	Refractories
Emulsion Hardeners	Tanning
Flexible printing	Textile Preservatives
Fungicides	Textile Printing and Dyeing
Gas absorbers	Wash Primers
High temperature Batteries	Wood Preservatives
Magnetic Tapes	

alum [Cr(III)] for tanning leather, pigments and wood preservatives (sodium dichromate), consume about 15% of the chromium produced. About 4% is converted into chromic acid and used for electroplating or as an oxidant. Table 5 shows the major uses of chromium chemicals ^[20].

Chromium in Vegetation

Concentrations of Cr in plants are extremely low due to lack of plant-available form in most soils. Various authors carried out experiments to observe the Cr uptake by plants by adding various Cr compound to soils. It was shown that recovery of added Cr by plants is extremely inefficient. Cary et al. ^[21] added up to 1% chromium as Cr(OH)₃ to grow wheat (*Triticum aestivum*), alfalfa (*Medicago sativa*) and buckwheat (*Fagopyrum esculentum*). This experiment showed that even at the highest Cr(OH)₃ level, the Cr concentration in wheat grain did not increase but there was some increase in leaves and stems. Alfalfa and buckwheat did have some increases in chromium concentration. In solution culture, rice plants (*Oryza sativa*) behaved in the same way. 95% Cr was retained on the root with less than 1% being translocated to the leaf ^[22].

Distribution and Behaviour of Cr in Aquatic Environment

Naturally occurring chromium concentrations in water arise from mineral weathering processes, soluble organic chromium, sediment load and precipitation. Chromium will also be present as a result of industrial pollution and is generally inseparable.

Table 6 : Chromium in river water in Malaysia ^[25]

State	River	Chromium ($\mu\text{g/l}$) Concentration
Kedah	Merbok	0.8
Sabah	Kalabakan	0.2
Sabah	Silabukan	0.2
Sabah	Kaya	0.2
Sabah	Kinabatangan	0.2
Sabah	Segama	0.2
Sabah	Kalumpang	0.2
Sabah	Tawau	0.2
Sabah	Umas-Umas	0.2
Sabah	Putatan	0.148
Johor	Endau	0.126
Sabah	Labok	0.095
Sabah	Membakut	0.05
Sabah	Papar	0.05
Pahang	Mentiga	0.05

Chromium in Streams and Rivers

Chromium is present in soluble and insoluble forms in river water. Most of the soluble chromium is present as hexavalent chromium which only contributes a few percent of the total. Chromium (III) is mostly present in suspended solids as organics, minerals and occluded oxides. Gibbs ^[23] reported the solution phase concentration in the Amazon River and in the Yukon River is as 2.0 and 2.3 $\mu\text{g/l}$, respectively. These two rivers contain the flows from watersheds of a wide variety of mineral containing soil and rocks. In another study, National Research Council of Canada ^[24] found that the concentration of chromium in 95.9% of the samples from natural streams and river water in Canada was less than 10 $\mu\text{g/l}$. Table 6 shows data for Malaysian rivers reported by The Department of Environment, Malaysia ^[25].

Chromium in Wastewater

Major content of chromium in water bodies comes from industrial and domestic wastewater. Industrial sources is known to contribute 68% of chromium in the influent to sewers in New York, USA. Chromium containing effluents are released by following activities: metal plating, anodizing, ink manufacture, dyes,

pigments, glass, ceramics, glues, tanning, wood preserving, textiles and corrosion inhibitors in cooling water. Both Cr(III) and Cr(VI) can be present in these effluents. Cr(VI), however, predominates in raw effluent from plating works [26]. Survey by Teh [27], involving 54 metal finishing premises located in the Klang valley around Kuala Lumpur, Malaysia, showed that the concentration of Cr(VI) was 6.6 mg/l and for Cr(III) was 94 mg/l. These values exceeded the Standard B of Environmental Quality (Sewage and Industrial Effluent) Regulation (1979) discharge limits of Malaysia which are 0.05 mg/l and 1.0 mg/l respectively.

Toxicity of Chromium

Effect of Chromium on Marine Organisms

Hexavalent Cr compounds are more soluble and relatively stable in marine waters than trivalent forms which are less soluble and readily form complexes with both organic and inorganic materials. Natural level of chromium in oceanic waters are approximately 0.04 µg/l.

Marine Fauna

Table 7 shows the acute toxicity (LC50) of hexavalent chromium Cr on marine fauna. The 96-h LC50 values show considerable interphyletic variation. The most sensitive phylum appears to be the annelids [28].

Table 7 : Acute toxicity (LC50) for hexavalent chromium [28]

Fauna	Chemical form	Duration of exposure	LC50 (µg/l)
Annelids			
<i>Capitella capitata</i>	Chromium trioxide	96 h	5000
<i>Neanthes arenaceodentata</i>	Potassium dichromate	96 h	3100
<i>Ctenodrilus serratus</i>	Chromium trioxide	96 h	4300
<i>Nereis virens</i>	Potassium chromate	96 h	2000
Crustaceans			
<i>Acartia clausi</i>	Potassium dichromate	96 h	6600
<i>Tigriopus japonicus</i>	Potassium dichromate	96 h	17200
<i>Mysidopsis bigelowi</i>	Potassium dichromate	96 h	4400
Fish			
<i>Fundulus heteroclitus</i>	Potassium chromate	96 h	91000
<i>Menidia menidia</i>	Potassium dichromate	96 h	20100

Toxicity data for trivalent and marine fauna are somewhat limited. Table 8 shows acute toxicity values for one species of mollusca and one species of crustacean [28].

Table 8 : Acute toxicity (96-h LC50) for trivalent chromium [28]

Fauna	Chemical form	LC50 (mg/l)
<u>Mollusca</u>		
<i>Crassostrea virginica</i>	Chromic chloride	10.3
<u>Crustacean</u>		
<i>Sosarma haomatochoir</i>	Chromic chloride	56.0

Marine Flora

Information on the effects of chromium on marine flora are limited to the inhibition of photosynthesis in a single species, the giant kelp *Macrocystis pyrifera*. It has been reported that 50% inhibition of photosynthesis occurs in a four day exposure to 5000 µg/l of chromium and 10 to 20% inhibition in a five days exposure to 1000 µg/l of chromium [28]. Holibaugh et al [29] studied the effect of hexavalent chromium on the marine phytoplankton, *Thalassiosira aestivalis*. It has been found that, inhibition of growth takes place when the chromium concentration exceeds 1000 nM (about 52 µM/l). Study on marine microflora demonstrated that the growth of phytoplankton *Asterionella japonica* and *Diogenes spp.* was inhibited at chromium levels of 40,000 µg/l and 3200 to 6400 µg/l respectively.

Effect of Chromium on Freshwater Organisms

The movement of Cr (VI) is easier than Cr (III) across biological membranes, unless its net charge is decreased by complexation. Cr (III) is described as more toxic (in terms of 96-h median lethal concentration) than Cr (VI) and the toxicity of Cr (III) is greater in softwater [30]. Chromic salts and dichromates show more toxic effect to fish than chromates [28].

Toxicity to Fish

Table 9 shows the acute toxicity of hexavalent chromium to freshwater fish in terms of 96-h LC 50. The toxicity of chromium not only depends on the particular species involved, but also shows greater effect in soft water, at low pH and high temperatures.

Table 9 : Acute toxicity of hexavalent chromium to freshwater fish ^[28]

Species	Conditions	96-h LC50 (mg/l)
Rainbow trout	mean weight 25 g pH 7.8	65.5
	pH 6.5	20.2
	Soft water	32
	Hard water	69
Silver salmon	Soft water	> 100
Fathead minnow	10°C	52
	25°C	37
Bluegill	Soft water	113
	Hard water	133

Trivalent chromium also shows a greater effect with water softness. Soft water enhances toxicity as compared with hard water. Table 10 shows the acute toxicity of trivalent chromium to fresh water fish.

Table 10 : Acute toxicity of trivalent chromium to fresh water fish ^[28]

Species	Conditions	96-h LC50 (mg/l)
Fathead minnow	Soft water	5.07
	Hard water	67.4
Bluegill	Soft water	7.46
	Hard water	71.9
Goldfish	Soft water	4.10
Guppy	Soft water	3.33

Toxicity to Invertebrates

Data on fresh water invertebrates indicate that under conditions of short term exposure to hexavalent chromium in most cases, a minimum concentration between 4 mg/l and 60 mg/l is required to cause harm. The acute toxicity of trivalent chromium appears to be similar to hexavalent chromium in the concentration range of 2 mg/l to 64 mg/l. Table 11 shows the acute values (96-h LC 50) for chromium ^[30].

Toxicity to Plants

The effect of chromium on aquatic plants is shown in Table 12. Hexavalent chromium as low as 10 µg/l reduced growth of the algae, *Chlamydomonas*. The higher plant, water millfoil had root growth inhibited by 50% by hexavalent chromium at 1.9 mg/l and trivalent chromium at 9.9 mg/l.

Table 11 : Acute values (96-h LC50) for chromium ^[30]

Species	Hardness (mg/l as CaCO ₃)	LC50 (µg/l)
<i>Hexavalent chromium</i>		
<i>Philodina acuticornis</i>	25	3,100
	81	15,000
<i>Physa heterostropha</i>	45	17,300
	171	31,600 - 40,600
<i>Gammarus psedolimnaeus</i>	45	67
<i>Trivalent chromium</i>		
<i>Nais sp</i>	50	9,300
<i>Amnicola sp.</i>	50	8,400
<i>Daphnia magna</i>	48	2,000
	99	27,400

Table 12 : Plant values for chromium ^[30]

Species	Effect	Chromium concentration (µg/l)
<i>Hexavalent chromium</i>		
<i>Navicula sominulum</i>	50% growth reduction	187 - 308
<i>Chlamydomonas reinhardi</i>	Reduction in growth	10
<i>Myriophyllum spicatum</i> (<i>Eurasian watermillfoil</i>)	50% root weight inhibition	1900
<i>Trivalent chromium</i>		
<i>Myriophyllum spicatum</i>	50% root weight inhibition	9900

Effect of Chromium on Human Health

There are three different routes of entry for chromium into the human body. Gastro-intestinal route is the most important in physiological conditions, while in occupational exposure the airways are more important route of entry and uptake. In pathological conditions, uptake through skin is more significant. Valency state of chromium compounds, water solubility, acidity of gastric juice and the passage time through the tract are the factors which control the uptake of chromium in gastro-intestinal tract. Uptake in the airways is influenced by the particle size distribution of the inhaled aerosol and on the factors which govern the clearance time from the lungs ^[31].

Ingestion of more than 3 g of chromic acid is considered as being lethal in adult human ^[31]. It caused vomiting immediately after ingestion which persisted for 24 hours, followed by diarrhoea which persisted for 3 days. Haemorrhagic diathesis, epistaxis and haemorrhages were observed after one week. Clinical signs shows Necrosis of renal tubulary and liver occurred on second day itself. Fatal cases of chromic poisoning have also been reported. Death followed 1-9 days after chromate ingestion and the patients suffering from convulsions during their final stages of their illness.

Inhaled aerosols which transport chromium containing compounds of low water solubility are deposited in the airways. Particles larger than 5 µm MMAD (Mass Median Aerodynamic Diameter) are deposited in the upper airways, particles between 2-5 µm (MMAD) mainly in bronchial tree, and also the smaller particles, below 0.5 µm in the alveolus region ^[32]. Bronchial asthma due to inhalation of chromate dust or chromic acid fumes has been reported. Chromium compound also may cause damage to the skin. The chromium reactions of the skin are of two categories, i.e., primary irritant reactions, that is chrome ulcers and allergic contact dermatitis. The primary irritant skin changes are corrosive reactions from certain chromium compounds ultimately causing ulcers. Allergic contact dermatitis is mainly of occupational origin, which presents as a dry and infiltrated, red skin change interrupted by periods of exacerbation with weeping eczema and a tendency of spreading to other areas than the original contact ^[33]

Carcinogenic Effects

Chromium compounds are also known for their carcinogenic effect especially when long term exposure is involved. Increased incident of cancer in the respiratory organs being reported among chromate workers. Inhalation of chromium in the form of dichromates also shows carcinogenic effect in human. Study on workers of U.S. chromate pigment plant by Equitable Environmental Health in 1976 showed an excess risk of respiratory cancer. In another study on workers from die casting and electroplating plant, Silverstein et al. found an approximately twofold proportional excess of deaths due to cancer of the respiratory system.

Recommended Environmental Quality Standards (EQS)

Environmental quality standards recommended by Water Research Centre^[28] are given in Table 13. The values given here are based on chemistry and behaviour of chromium in the environment and its effect on human consumers, fish and other biota and agricultural crops.

Table 13 : Environmental Standard Quality by ^[28] (*mandatory values)

Use	Average concentration (µg/l)
<u>Freshwater</u>	
Direct abstraction to potable supply	50*
Protection of fresh water fish : Salmonid	
Total hardness < 50	5
50 - 100 mg CaCO ₃ /l	10
100 - 200	20
> 200	50
<u>Coarse fish</u>	
Total hardness < 50	150
50 - 100 mg CaCO ₃ /l	175
100 - 200	200
> 200	250
Irrigation of crops	2000
Abstraction for food processing industry	50
Bathing and contact water sports	500
<u>Saltwater</u>	
Protection of saltwater fish and shellfish	15
Protection of other saltwater life and associated non-aquatic organisms	15
Bathing and contact	500

THE EFFECT OF NICKEL

The major uses of refined nickel in industry include electroplating, alloy production and fabrication, the manufacture of nickel-cadmium batteries and electronic components, and the preparation of catalysts for hydrogenation of fats and methanation.

The waste generated from these industries contain nickel in various concentrations. In absence of proper treatment and disposal methods, nickel contamination in soil or water would occur, and cause toxic exposure to living organisms ^[34].

Nickel in Vegetation

Nickel is a non-essential trace element that occurs in trace amounts in most plants. Where nickel exceeds threshold limit, inhibitory effects take place. The most critical factor in evaluating the impact of nickel on an ecosystem is the uptake and accumulation of nickel in various organs of plants and animals. The mechanism of absorption of nickel by plants is influenced by the amount and form of nickel in the soil. It also affects the plant growth and, to the extent that plants serve as a source of food for higher organisms, in relation to the entire food chain [35]. The transfer of nickel from the soil to the plant depends primarily on the following factors :

Soil pH

The uptake of nickel is enhanced by the reduction in pH, especially below 6.5. This is caused by the breakdown of iron and manganese hydroxides, which form stable complexes with nickel. The release of nickel from these sites facilitates the movement of nickel into the plant root and thereby accounts for higher levels of accumulation.

Metallic Interactions

Metallic interaction has an important role on nickel uptake. Interactions among metals, are mutual or reciprocal in nature that affect the plant growth (Olsen, 1972).

Concentration of Nickel.

Plants accumulate nickel and other heavy metals depending on their availability in the soil.

Accumulation of Nickel in Plants

The nickel content of vegetation is usually below $1\mu\text{g/g}$ on dry weight basis except where nickel rich substrates such as serpentinite are involved. For example, Vanselow reported 0.05 to $5\mu\text{g/g}$ for field grown crops and natural vegetation. Conner et al [37] reported mean values in the range of 0.20 to $4.5\mu\text{g/g}$ for nearly 2000 specimens of field crops and natural vegetation from United States. Although the concentration of nickel in vegetation growing on 'normal' soils seldom exceeds $5\mu\text{g/g}$, this is not valid when ultrabasic substrates such as periodotite or serpentinite are involved. The nickel content in dried vegetation from serpentinite areas often is as high as $100\mu\text{g/g}$. The discovery of Haselhoff [38] on the toxicity of nickel to vegetation, generated research interest among scientists. The toxicity of nickel in plants is characterized by chlorosis of leaves, stunting of roots

and deformation of various plant organs^[35]. The poisoning of enzymes is considered to be the most significant toxic action of this element^[39].

Distribution and Behaviour of Nickel in the Aquatic Environment

The behaviour of nickel in the aqueous environment is governed by its reaction with both soluble species and particulate materials. Complexation is possible which form soluble nickel-organic and nickel-inorganic species. Interaction with solid phases may occur by any of the following mechanisms:

1. direct adsorption on fine grained inorganic particles such as clays
2. adsorption to, or coprecipitation with, hydrous ferric and manganese oxide which may then be sorbed to clay surfaces
3. complexation or adsorption with natural organic particles (e.g. detritus, algae, bacteria)
4. ion-exchange with colloids
5. direct precipitation

Nickel in Streams and Rivers

Several studies report the observed concentration of nickel in flowing river water^[35]. Table 14 shows data for Malaysian rivers, reported by The Department of Environment, Malaysia^[40]. In the major rivers of the world the forms of nickel have been estimated and is given in Table 15^[23,41].

Nickel in Lakes

The concentration of nickel in lakes, is reflected by the nickel contents of the surrounding bedrock unless modified within the lake. The modification of concentration, occurs in lakes due to: (i) detritus materials become incorporated in lake sediments and undergo diagenesis or (ii) because of discharge of industrial/municipal wastes containing heavy metals. Influent having a nickel concentration of 1 to 3 µg/l is not considered to be serious source of pollution for lake waters.

Nickel in Estuaries

In estuaries, the higher concentrations are caused by association of nickel with fine grained particles, organic matters, iron and manganese hydroxide. Trefry and Presley found that nickel in suspended matter in river waters does not vary much from that in suspended matter in estuary^[42]. This similarity argues against any significant desorption of nickel from the suspended matter, as the sediment changes. However, nickel in the delta sediments is significantly lower than in

Table 14 : Nickel in river water in Malaysia ^[40]

State	River name	Nickel concentration (mg/l)
Terengganu	Kemaman	0.9000
Johor	Benut	0.1930
Sabah	Putatan/Moyong	0.0762
Johor	Sedeli Kechil	0.0650
Johor	Sedeli Besar	0.0500
Sarawak	Miri/Lutong	0.0500
Sabah	Labok	0.0400
Sabah	Sugut	0.0395
Johor	Batu Pahat	0.0317
Johor	Tukang Batu	0.0310
Sabah	Kinabatangan	0.0250
Johor	Endau	0.0220
Johor	Johor	0.0182
Sabah	Silabukan	0.0100
Sabah	Mengalong	0.0100
Sabah	Umas-Umas	0.0100

Table 15 : Forms of nickel in the major rivers of the world ^[23,41]

Form	Percentage (%)
Dissolved	0.5
Adsorbed	3.1
Precipitated coating	47.0
Organic matters	14.9
Crystalline materials	34.4

the suspended matter, which shows that desorption or postdesorptional migration of nickel occurs.

Nickel in Wastewater

Major content of nickel in water bodies comes from industrial and municipal wastewater. Table 16 shows data from a study by Klein et al., on New York City wastewater collection ^[43].

Table 16: Nickel in various wastewater^[43]

Sources	Percentage of Nickel (%)
Electroplaters	62.0
Other industrial units	3.2
Runoff	9.8
Residential	25.0

Table 16 shows that electroplating plants are the main source of nickel in wastewater and residential sources contributing 25% of the total nickel in wastewater. Another survey by Teh, involving 54 metal finishing premises located in the Klang Valley, showed that the concentration of nickel was as 94.0 mg/l^[27]. These value exceeded the Standard B of Environmental Quality (Sewage and Industrial Effluent) Regulation 1979 discharge limits of Malaysia which is 1.0 mg/l.

Toxicity of Nickel

Effect of Nickel on Marine Organisms

Nickel occurs in aquatic environment mainly in the form of divalent cation. Nickel enters the marine environment both as result of natural mineralisation and anthropogenic factors. Usually the level of nickel in seawater from locations unaffected by mineralisation or pollution is less than 1.0 µg/l.

Marine Fauna

Table 17 shows the acute toxicity of nickel to marine fauna. The cases of 12 invertebrate species and 2 vertebrate (fish) species are presented. The toxicity of nickel presented as 96-hour (LC50) acute values, is as follows^[44]. A study by Timourian and Watchmaker^[45] shows that the lowest nickel concentration reported to produce an adverse effect in a marine animal was 58 µg/l. It was found that, this concentration delayed development of embryos of the sea urchin, *Lytechinus pictus*.

Marine Flora

Clendenning and North^[46] found out that for macroalgae, nickel concentration of 2000 µg/l caused 50% inactivation of photosynthesis in the *Macrocystis pyrifera* (brown algae). Skaar et al^[47] showed that a nickel concentration of 1000 µg/l would reduce the growth of *Phaeodactylum tricornutum* (phytoplankton). In another study on mixed culture of phytoplankton, Hollibaugh et al observed growth inhibition at the concentration of 581 µg/l^[29].

Table 17 : Acute toxicity (96-h LC50) of Nickel (as chloride) to marine fauna^[44]

Species	LC50 (µg/l)
Annelida	
<i>Ctenoderilus serratus</i>	17000
<i>Neanthes arenaceodentata</i>	49000
<i>Nereis virens</i>	25000
Mollusca	
<i>Nassarius obsoletus</i>	72000
<i>Mya arenaria</i>	320000
<i>Mercinaria mercinaria</i>	320
Crustacea	
<i>Acartia clausi</i>	2080
<i>Nitocra spinipes</i>	600
<i>Heteromysis formosa</i>	152
<i>Mysidopsis bigelowi</i>	634
<i>Mysidopsis bahia</i>	508
Echinodermata	
<i>Asterias forbesi</i>	150000
Fish	
<i>Fundulus heteroclitus</i>	350000
<i>Menidia menidia</i>	7960

Effect of Nickel on Freshwater Organisms

Acute Toxicity of Fish

The toxicity of nickel for fresh water organisms depends on animal species, water hardness, pH and other conditions^[48]. A 96- hour median lethal concentration (96-h LC) of nickel from 2.5 mg Ni/l to 110 mg/l were reported for various species of fish. Among the different species of fish, rainbow trout was apparently one of the most resistant species. A study by US Environment Protection Agency showed some adverse effects on two species of fresh water fish: rainbow trout and fathead minnow^[30]. It appears, however, that the adverse effect can be caused by the exposure for extended periods in both species, for the concentration of nickel greater than 0.4 mg/l to 0.5 mg/l in hardwaters.

Therefore, it is recommended that for the protection of fish in such waters (250 mg/l as CaCO₃), the average concentration of nickel should not exceed 200

µg/l. In soft waters (44 mg/l as CaCO₃) embryos and larvae of fathead minnow were adversely affected at 0.11 mg Ni/l and, therefore, in such waters a maximum average concentration of 50 µg Ni/l is recommended.

Toxicity in Freshwater Invertebrates

An adverse effect was observed for the lowest concentration of 0.03 mg/l for an invertebrate. This will cause 16% impairment in reproduction in *Daphnia magna* in soft water (hardness 45 mg/l as CaCO₃) over an exposure period of 21 days^[49]. *Daphnia magna* indicate acute LC 50 to be larger with a greater degree of water hardness^[30]. In another study, Buikema et al^[50] gave a probit-derived 96 - hr LC50 of 2.6 mg Ni/l for the rotifer *Philodina acuticornis*.

Toxicity in Freshwater Plants

Adverse effects of nickel in algae can be found with the concentrations between about 50 µg/l and 700 µg/l^[51]. Another study on *Scenedesmus sp. drew* attention because the species was not affected by a nickel concentration of 3.0 mg/l and categorized as metal tolerant strain^[44]. The data for *Lemna*, a higher flowering plant also show that the level proposed for the protection of algae could be adequate for the protection of higher plants^[44].

The Effect of Nickel on Human Health

Since nickel can be found in soil and water, it is available in natural foods and water. Nickel can be found in vegetables, fruits and grains. The nickel content of plants depends on the quality of the soil in which they grow and the ability of a plant to incorporate nickel.

There are two significant routes of entry of nickel into the human body, namely inhalation and ingestion. The inhaled nickel may be transported into the blood and excreted, or it may be retained in the lung. In a study on nickel content in blood plasma among workers in a nickel refinery, Hogetveit and Barton found 0.74 µg/100 ml, 0.6 µg/100 ml and 0.42 µg/100 ml among these who were working in electrolysis, furnace and control group section respectively^[52]. Solubility is the primary factor which determines the availability of nickel in the lungs. Nickel oxide or metallic nickel, which is insoluble in body fluids, may be retained for a long period.

Nickel, most often found as Ni²⁺, can form co-ordination complexes with organic molecules. Complexes with amino acids through binding with carbonyl and alpha amino acid groups are common for nickel and it has high affinity for sulphur^[53].

Among nickel compounds, the most acutely toxic to man is nickel carbonyl. According to Sunderman ^[54] and Vuopala et al ^[55], clinical symptoms of acute nickel carbonyl poisoning include frontal headache, nausea, vomiting, insomnia and irritability. Persistent symptoms include, constrictive chest pains, dry cough, hyperpnea, cyanosis, occasional gastrointestinal disturbances, sweating, visual disturbances and severe weakness. Other nickel forms also cause adverse respiratory effects on man. Inhalation of nickel sulphate aerosols, has been found causing chronic rhinitis and nasal sinusitis in Russian nickel platers ^[35]. Many authors have reported nickel as a carcinogenic metal. Table 18 shows a possible relation between exposure to nickel and the incidence of cancer ^[35].

Table 18 : Possible relation of cancer and nickel compounds ^[35]

Compounds	Population	Nature of tumor
Ni carbonyl, Ni ₃ S ₂ dust, nickel copper oxide	Nickel refinery	Nasal sinus cancer, lung cancer, other neoplasma
Nickel ore dust	Nickel refinery	Nasal cavities, larynx, lungs
Ni ₃ S ₂ , NiO, Ni ₂ O ₃ , Ni(CO) ₄ , NiSO ₄ , NiCl ₂	Nickel refinery	Pulmonary and nasal cavity cancers
Nickel carbonyl, nickel ore dust	Nickel mining, nickel refinery	Bronchii and upper respiratory organs
Nickel	Nickel refinery, metal workers	Squamous cell and oat cell carcinoma
Nickel carbonyl, nickel oxide, nickel subsulfide	Nickel refinery	Nasal cavity and lung cancer

It has been found that nickel also may cause dermatitis. 'Nickel itch', a disease among workers handling nickel salts was once common, especially in hot or humid environments. Nickel was the most common allergen tested by the North American Contact Dermatitis Group ^[56]. A study showed that, 11% in a group of 1200 persons had positive patch test for nickel.

Recommended Environmental Quality Standards (EQS)

Environmental quality standards recommended by Water Research Centre, are given in Table 19 ^[44]. The values given are based on chemistry and behaviour of nickel in the environment and effects of nickel on human, fish, other biota, agricultural crops etc.

Table 19: Environmental Standard Quality ¹⁴⁴¹

Use	Average concentration (µg/l)
<i>Fresh water</i>	
Direct abstraction to potable supply	50*
Protection of fresh water fish	
Total hardness < 50	50
as mg CaCO ₃ /l 50 - 100	100
100 - 200	150
> 200	200
<i>Protection of other freshwater life and associated non-aquatic organisms</i>	
Total hardness < 50	8
as mg CaCO ₃ /l 50 - 100	20
100 - 200	50
> 200	100
Irrigation of crops	150
Abstraction for food processing industry	50*
Bathing and contact water sports	500
<i>Saltwater</i>	
Protection of saltwater fish and shellfish	30
Protection of other saltwater life and associated non-aquatic organisms	30
Bathing and contact	500

* indicates mandatory values ¹⁴⁴¹.

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